

# DIVISION S-8—NUTRIENT MANAGEMENT & SOIL & PLANT ANALYSIS

## Spatial Variability of Grain Cadmium and Soil Characteristics in a Durum Wheat Field

J. Wu, W. A. Norvell\*, D. G. Hopkins, and R. M. Welch

### ABSTRACT

The accumulation of Cd in edible crops is undesirable because of potential risks to human health. Agronomic efforts to lower Cd in foods will be more effective if we understand the extent and causes of spatial variability of Cd in crops in the field. The primary objective of this study was to characterize the spatial variability of grain Cd and eight soil characteristics in a field of durum wheat [*Triticum turgidum* L. subsp. *durum* (Desf.) Husn.] in northeastern North Dakota. A rectangular area of about 0.5 ha was selected to provide a range in several soil characteristics that are reported to influence Cd uptake by plants. These included chelate-extractable Cd, total soil Cd (Cd<sub>t</sub>), pH, cation-exchange capacity (CEC), organic C (OC), and soluble Cl, S, and Na. Location data and paired samples of soil and durum grain were collected at 124 sites. Semivariograms showed that the variations of grain Cd and most soil properties were strongly spatially dependent, with range distances that varied from about 30 to 55 m. A spherical model was fitted successfully to variograms for all characteristics. Maps of grain Cd and soil characteristics were generated by interpolating among measured values by block kriging. Visual and statistical comparisons of maps showed that grain Cd was distributed similarly to measures of soil salinity, especially to the logarithm of soil Cl. Locations with somewhat poorly drained soils, which contained elevated Cl, produced grain with much higher Cd. Our results suggest that knowledge of the spatial distribution of soil characteristics, especially salinity, should be helpful in developing or applying agronomic practices to reduce Cd in durum grain.

CADMIUM is a heavy metal that is present in all soils, usually as a trace constituent. Soils are the main source of Cd in plants, and plant-derived foods are the main source of Cd in human diets (Wagner, 1993). Accumulation of Cd in edible crops is undesirable because of potentially harmful effects on health. The concentrations of Cd in food crops are subject to regulation by national and international agencies. If adopted, the limits now being considered (0.1 mg kg<sup>-1</sup> as a guideline level and 0.2 mg kg<sup>-1</sup> as the maximum level) for Cd in small grains (Council of Europe, 1994; Codex Alimentarius Commission, 1999) are likely to restrict the marketability of durum wheat, because this crop tends to accumulate more Cd than most other small grains (Wolnik et al., 1983; Chaney et al., 1996; Clarke et al., 1997).

Durum wheat is an important and valuable crop in many parts of the world, including the upper Great Plains

of North America. A total of about 1.5 million ha of durum is planted annually in the USA, with about 80% concentrated in northern North Dakota. In some locations, durum wheat grain may easily accumulate enough Cd to approach or exceed the concentration limits being considered by international regulatory agencies (Chaney et al., 1996; Norvell et al., 2000). Our understanding of the factors that regulate Cd uptake by durum wheat is still quite limited, but it is clear that the concentration of Cd in durum wheat grain is influenced by differences in geographic location, soil conditions, cropping season, and cultivar (Li et al., 1994; Clarke et al., 1997; Norvell et al., 2000). Among the soil characteristics that are known or suspected to influence uptake of Cd by plants are pH, CEC, clay content, organic matter content, carbonate content, salinity (especially Cl), and the amount and form of soil Cd (Li et al., 1994; McLaughlin et al., 1994; Clarke et al., 1997; Norvell et al., 2000).

Relatively little is known about the spatial variability of Cd in grain or available Cd in soil. However, this information will be needed to develop and apply agronomic practices to lower the accumulation of Cd by durum wheat or other crops. Site-specific management, in particular, requires knowledge of the spatial distribution of relevant soil factors within the scale of field operations (van Es, 1993; Cahn et al., 1994; Camberdella et al., 1994; Borges and Mallarino, 1997). Substantial field scale variability in crop and soil Cd seems probable for several reasons. First, field-scale variability is common for many soil and crop characteristics (Trangmar et al., 1985; Webster, 1985; Warrick et al., 1986). Second, our previous results (Norvell et al., 2000) showed that concentrations of Cd in durum grain from a single field can vary about as widely as the range reported for the entire durum-producing region of the northern Great Plains (Chaney et al., 1996; Grant et al., 1999). Third, a low density geochemical survey of soils of the northern Great Plains indicated that >95% of the variability in Cd<sub>t</sub> was found at distances <20 km (Garrett, 1994).

Geostatistical methods have been widely used to document the spatial variability of soil properties (Trangmar et al., 1985; Webster, 1985; Warrick et al., 1986; West et al., 1989; Cahn et al., 1994; Camberdella et al.,

J. Wu, Dep. Crop and Soil Sci. Cornell Univ., Ithaca, NY 14853; W.A. Norvell\* and R.M. Welch, U.S. Plant, Soil & Nutrition Lab., USDA-ARS, Tower Rd., Ithaca, NY 14853; D.G. Hopkins, Dep. Soil Sci., North Dakota State Univ., Fargo, ND 58105. Received 13 Oct. 2000. \*Corresponding author (wan1@cornell.edu).

Published in Soil Sci. Soc. Am. J. 66:268–275 (2002).

**Abbreviations:** Cd<sub>g</sub>, concentration of Cd in grain; Cd<sub>dtpa</sub>, DTPA-extractable Cd; Cd<sub>t</sub>, total Cd; CEC, cation-exchange capacity; CV%, coefficient of variation (%); DTPA, diethylenetriaminepentaacetic acid; ICPEs, inductively-coupled argon plasma emission spectrometry; LnCl, natural logarithm of water-extractable Cl; LnS, natural logarithm of water-extractable SO<sub>4</sub>-S; LnNa, natural logarithm of soluble Na extracted by DTPA; OC, organic C; SD, standard deviation.

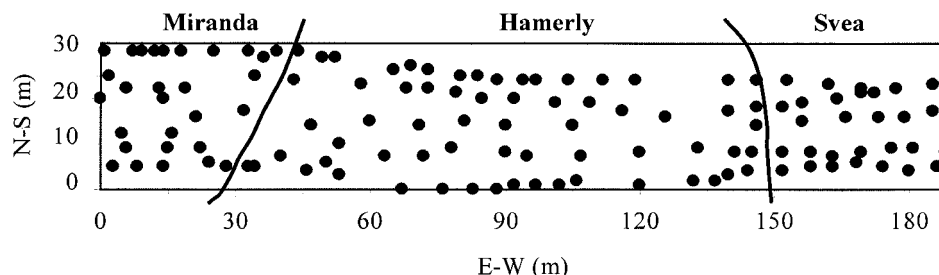


Fig. 1. Layout of sampling points on the field soil map (from M.D. Sweeney, Unpublished 1989; Soil Map [1:3960] of Langdon Research Center. Dep. Soil Science, North Dakota State University, Fargo, ND). Three soils were mapped in the area studied: Miranda (fine, smectitic, frigid Leptic Natrustolls); Hamerly (fine-loamy, mixed, superactive, frigid Aeric Calciaquolls); and Svea (fine-loamy, mixed, superactive, frigid Pachic Hapludolls).

1994). Geostatistical methods have been applied also to evaluate the spatial variations of plant properties, such as crop yield (Bhatti et al., 1991; Stein et al., 1997; Timlin et al., 1998), and the uptake of P and K by corn (*Zea mays* L.) or soybean [*Glycine max* (L.) Merr.] (Borges and Mallarino, 1997). The objectives of this study were to: (i) characterize the spatial variability of grain Cd and eight soil characteristics in a field of durum wheat in northeastern North Dakota, (ii) develop maps of these characteristics and assess the spatial correlations among them, and (iii) explore associations between these mapped characteristics and the soil types present.

## MATERIALS AND METHODS

### Field Characteristics and Sampling Procedures

Grain and soil samples for this study were obtained by Norvell et al. (2000) from a field of durum wheat at the Langdon Research & Extension Center of North Dakota State University, located in Cavalier County in northeastern North Dakota. This field was selected because the soils provided a range in values for several characteristics (i.e., pH, CEC, OC, and salinity) that are often reported to influence Cd uptake by plants. The samples were collected in mid-August of 1997, when the durum cultivar Munich was close to maturity. Each sample pair of grain and soil consisted of about seven heads of wheat and 1 kg of soil taken from the 0- to 15-cm depth in the upper root zone of the sampled plants.

Samples of soil and grain were collected from 124 locations within a roughly rectangular area of 186 by 31 m<sup>2</sup>. The sample sites were unevenly distributed along several traverses across this area (Fig. 1). A more regular distribution of sites was impractical, because several areas of the field did not contain adequate crop to permit collection of grain. The coordinates of each site were recorded with a Precision Lightweight Global Positioning System (GPS) Receiver (PLGR+96 Federal HNV-560C<sup>1</sup>, Rockwell International Corporation, Cedar Rapids, IA, 1996), which continuously tracks signals from up to five NAVSTAR satellites. Experience with this GPS unit suggests an overall uncertainty in coordinates of about 2 to 3 m, but with a lower uncertainty of about 1 m among nearby sites measured at close times. This level of uncertainty was considered acceptable for sites separated by distances of generally 5 to 185 m, and for changes in characteristics expected to occur over distances of many meters.

A detailed soil map of the field [M.D. Sweeney, unpublished

data, 1989; Soil Map (1:3960) of Langdon Research & Extension Center. Dep. Soil Science, NDSU, Fargo, ND] shows three soil map units within the area sampled (Fig. 1): Miranda (fine, smectitic, frigid Leptic Natrustolls), Hamerly (fine-loamy, mixed, superactive, frigid Aeric Calciaquolls), and Svea (fine-loamy, mixed, superactive, frigid Pachic Hapludolls) (NRCS, 2000). All of these soils developed on glacial drift (Simmons and Moos, 1990). The Miranda unit contains somewhat poorly drained, very slowly permeable, alkaline soils on typically flat sites. The Hamerly is a somewhat poorly drained, calcareous soil found typically on nearly level sites with slope of about 1%. The Svea soils are found on well-drained or moderately well-drained sites with slopes of about 3% or more. The presence of salinity in this field and in the local shallow groundwater is recognized (unpublished data, Langdon Research & Extension Center), although neither characteristic is diagnostic nor typical for the three mapped soil series. Quantitative data on site elevations were not collected, but visual observations indicate that the areas mapped as Miranda and Hamerly were nearly flat, while that mapped as Svea sloped gently upward to the east.

### Sample Processing and Measurements

Sample processing and analyses of soil and grain were described by Norvell et al. (2000) and are summarized here only briefly. All grain heads were dried and then threshed by hand. Subsamples of whole grain were digested in concentrated HNO<sub>3</sub>-HClO<sub>4</sub> acids and analyzed by inductively-coupled argon plasma emission spectrometry (ICPES). All soil samples were air-dried and passed through a 2-mm stainless steel sieve. Soil pH in water (1:1) was determined by glass electrode. Elements extracted by diethylenetriaminepentaacetic acid (DTPA) were determined according to the method of Lindsay and Norvell (1978), except that a 1:3 soil/solution ratio was used to obtain adequate filtrate for analysis. The filtrates were analyzed by ICPES for Cd and Na (DTPA-extractable Cd [Cd<sub>dtpa</sub>] and DTPA-extractable Na [Na<sub>dtpa</sub>], respectively). Water soluble Cl and SO<sub>4</sub>-S (extraction of 5 g of soil with 20 mL for 1 h) were determined by ion chromatography (DIONEX Ion Chromatograph, Dionex Corp., Sunnyvale, CA). Soil CEC and OC contents were measured according to the methods of Chapman (1965) and American Public Health Assoc. (1995), respectively. Concentrations of Cd<sub>t</sub> were measured by digestion with concentrated HNO<sub>3</sub>-HClO<sub>4</sub> on a hot plate, followed by dissolution of residues in aqua-regia, and analysis by ICPES (this digestion does not solubilize elements bound in silicate minerals, but it recovers nearly all Cd present in these soils [>92%, data not presented], and achieves detection limits [~0.02 mg kg<sup>-1</sup>] adequate to characterize these uncontaminated soils).

<sup>1</sup> Mention of proprietary product or vendors does not imply approval or recommendation by the USDA.

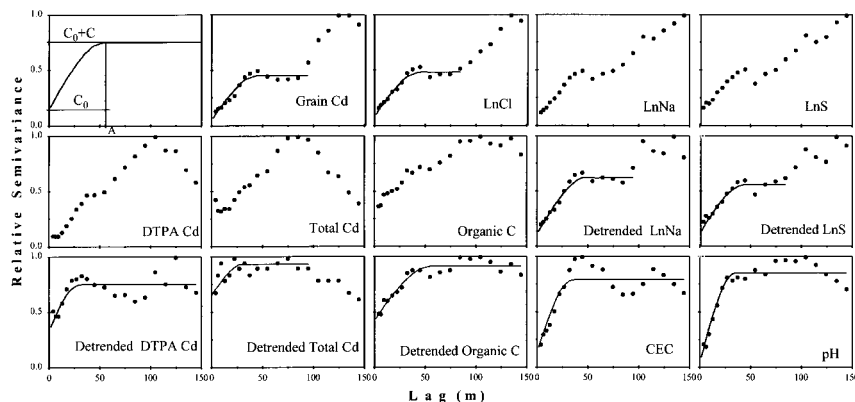


Fig. 2. Relative semivariance as a function of lag distance for nine characteristics of grain or soil in a field of durum wheat (the relative semivariance is the semivariance for a variable divided by its maximum semivariance). Semivariograms are shown for the concentration of Cd in durum grain (Grain-Cd), DTPA-extractable soil Cd (DTPA-Cd), quadratic model detrended DTPA-Cd, total soil Cd (Total-Cd), quadratic model detrended Total-Cd, natural log-transformed water-extractable Cl (LnCl), natural log-transformed water-extractable  $\text{SO}_4$  as S (LnS), linear model detrended LnS, natural log-transformed DTPA-extractable Na (LnNa), linear model detrended LnNa, pH, organic C (OC), linear model detrended OC, and cation-exchange capacity (CEC).

### Geostatistical Analysis

Spatial variability was evaluated with the aid of semivariograms, which were constructed and evaluated according to standard geostatistical methods (Journel and Huijbregts, 1978; Warrick et al., 1986; Goovaerts, 1997). When possible, the semivariograms were fitted with a spherical model:

$$\gamma(h) = C_0 + C [1.5(h/A) - 0.5(h/A)^3] \quad \text{for } h \leq A \quad [1]$$

$$\gamma(h) = C_0 + C \quad \text{for } h > A \quad [1a]$$

where  $C_0$ ,  $C$ ,  $A$ , and  $h$  are the nugget variance, structural variance, range, and lag distance (see idealized curve for the spherical model in the upper left panel of Fig. 2).

Fitted models for the semivariograms were used as the basis for kriging of variables meeting the assumption of second-order stationarity, i.e., the spatial covariance was finite and a function only of the lag distance between pairs of observations. For these variables, we performed block kriging with a block size of 1 by 1  $\text{m}^2$ , using the nearest 16 sampling points and a maximum searching distance equal to the range distance of the variable. We used GS<sup>+</sup> (v3.1 for windows, Gamma Design Software, Plainville, MI) for these geostatistical analyses. When a variogram showed clear evidence of trend, we attempted to model the trend with a second-order polynomial function (SAS Institute Inc., 1988; Goovaerts, 1997):

$$Z = a + bX + cY + dX^2 + eXY + fY^2 \quad [2]$$

where  $Z$  is the value of the modeled variable,  $X$  and  $Y$  are coordinates, and  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$ , and  $f$  are fitted coefficients. After the removal of the modeled trend from the original data, the variogram was recalculated using the detrended data. If the stationarity assumption was now satisfied, we performed kriging on the detrended data. Thorough explanations of geostatistical theory can be found in textbooks and monographs such as Journel and Huijbregts (1978), Warrick et al. (1986), or Goovaerts (1997).

### Map Analysis

The interpolated values of the variables were imported into ARC/INFO (ESRI Inc., 1994) to create maps. Correlation and regression analyses were conducted to measure the relationships between the mapped values of  $\text{Cd}_g$  and those of soil variables, using the interpolated values for each 1- $\text{m}^2$  cell ( $n = 5766$ ). These relationships among mapped variables may be

compared with those among the data for the original 124 sites from which the maps were derived. For the regressions, we assigned the soil maps as the source of explanatory (regressor) variables and the  $\text{Cd}_g$  map as the source of the dependent variable. Multiple-linear and nonlinear relations among maps were explored (Taylor, 1982; Stein et al., 1997). Overlay analysis between the field soil map and the  $\text{Cd}_g$  map or the maps of soil variables was performed to estimate mean values of the attributes within a map unit and quantify the differences among map units. We used ARC/INFO to complete the map analysis (ESRI Inc., 1994).

## RESULTS AND DISCUSSION

### Statistical Characterization of Data

The data set used for spatial analysis in this study was described in greater detail by Norvell et al. (2000). Their results are summarized in Table 1, and described briefly below for the convenience of readers. The mean for  $\text{Cd}_g$  in the 124 samples was  $0.182 \text{ mg kg}^{-1}$ , with a large range of about 15-fold between the minimum and maximum values. The statistical distribution of  $\text{Cd}_g$  was reasonably normal as shown by the values close to zero for skewness and kurtosis (SAS Institute Inc., 1988). Cadmium in soil was less variable. Soil  $\text{Cd}_{\text{dtpa}}$  and  $\text{Cd}_i$  varied only about 2.5-fold between their respective minimum and maximum concentrations. These distributions were only slightly skewed (skewness  $< 1$ ), and their medians were close to their means. The mean concentration of  $0.34 \text{ mg kg}^{-1}$  for  $\text{Cd}_i$  is similar to the mean of  $0.3 \text{ mg kg}^{-1}$  reported for agricultural soils in the USA (Holmgren et al., 1993) and soils of the northern Great Plains of the USA and Canada (Garrett, 1994). Concentrations of  $\text{Cd}_{\text{dtpa}}$  were generally about one third those of  $\text{Cd}_i$ .

Soil pH, OC, and CEC were distributed in an approximately normal fashion. Soil pH ranged from the slightly acidic value of 5.95 to the alkaline pH of 8.07, with a mean of 7.45. Soil OC and CEC varied by less than a factor of two. The CEC values were typical of soils in this region with a textural class of clay loam or silty clay loam (NRCS, 2000).

The variable but relatively high salinity of the area



**Table 1.** Summary statistics for grain Cd and selected soil characteristics in a durum wheat field ( $n = 124$ ).

Variable†	Cd <sub>g</sub>	Cd <sub>dtpa</sub>	Cd <sub>t</sub>	pH	OC	CEC	Cl	Na	S	LnCl	LnNa	LnS
	mg kg <sup>-1</sup> grain	— mg kg <sup>-1</sup> soil —			g kg <sup>-1</sup>	cmol <sub>c</sub> kg <sup>-1</sup>	— mg kg <sup>-1</sup> soil —					
Mean	0.182	0.109	0.34	7.45	29.6	31.4	189	600	707	4.29	6.00	5.81
Median	0.196	0.112	0.34	7.63	29.3	31.4	130	603	727	4.87	6.40	6.59
SD‡	0.080	0.019	0.06	0.50	3.8	2.5	244	418	524	1.68	1.07	1.77
CV%‡	44.0	17.5	17.5	6.8	12.7	8.1	130	70	74	39.1	17.8	30.4
Maximum	0.359	0.155	0.59	8.07	38.5	37.6	1700	1810	1940	7.44	7.50	7.57
Minimum	0.025	0.064	0.22	5.95	21.1	25.8	2	34	3	0.59	3.54	1.14
Skewness	-0.29	-0.45	0.75	-0.83	0.11	-0.01	3.09	0.39	0.23	-0.59	-0.91	-1.45
Kurtosis	-0.64	-0.25	1.65	-0.39	-0.51	-0.62	13.98	-0.62	-0.96	-0.77	-0.30	1.00

† Cd<sub>g</sub>, concentration of Cd in grain; Cd<sub>dtpa</sub>, DTPA-extractable Cd; Cd<sub>t</sub>, total Cd; OC, organic C; CEC, cation-exchange capacity; Cl, water-extractable Cl; Na, soluble Na extracted by DTPA; S, water-extractable SO<sub>4</sub>-S; LnCl, LnNa, and LnS are natural logarithms of Cl, Na, and S, respectively.

‡ SD, standard deviation; CV%, coefficient of variation. Original data were collected by Norvell et al. (2000).

studied is shown by the large range and high concentrations of Na, S, and Cl. The coefficients of variation (CV%) ranged from 70% for Na to 130% for Cl. The range of soil Cl was extremely large, from a low of 2 mg kg<sup>-1</sup> to a high of 1700 mg kg<sup>-1</sup>. The concentration of Cl was the only attribute with large skewness and kurtosis, showing that the distribution of this characteristic was far from normal. The large positive skewness for Cl reflects asymmetry in the distribution caused largely by a number of very high values. A natural logarithmic (Ln) transformation was applied to the data for Cl, Na, and S. This was done in part because Norvell et al. (2000) showed that the logarithmically transformed concentrations of Cl, Na, and S were more closely related to Cd<sub>g</sub> in this field than were their nontransformed concentrations. Another benefit of transformation is that distortion of the semivariance and other computed statistics by extreme values is reduced (Journel and Huijbregts, 1978; Goovaerts, 1997). After transformation, the skewness and kurtosis of Cl were greatly reduced, providing a more normally distributed population, but transformation did not improve the normality of the distribution of Na or S.

### Semivariogram Analysis

Semivariograms were prepared for all nine variables (Fig. 2). For the first lag distance, with an average separating distance of 3.7 m, the semivariances were calculated from 65 pairs of samples. For the rest of the lags, the semivariances were obtained from more than 100 pairs of samples. The semivariograms were limited to separation distances <150 m to avoid distortions in semivariance caused by the arbitrary restriction of site-pairs by the boundaries of the area sampled. Omnidirectional semivariograms were prepared, but it should be noted that, because of the rectangular shape of the site, these variograms are dominated by trends in the east-west direction. All of the variograms show a high degree of spatial dependency. None follow the simple classical shape for a second-order stationary variable, illustrating that the spatial dependencies of variables in this field were more complex than simple functions of separation distance. However, for most variables, the stationarity assumption was satisfied within a limited range of separation distances, a condition known as quasi-stationarity (Journel and Huijbregts, 1978), which permits geostatistical inferences within this range. Thus, for most vari-

ables, we were able to fit at least a portion of the experimental semivariogram with the spherical model (Eq. [1]), using the parameters listed in Table 2.

The semivariograms of Cd<sub>g</sub> and the natural logarithm of water-soluble Cl (LnCl) were very similar. Starting with a nugget variance of <0.1, the  $\gamma$  gradually increased as  $h$  increased up to about 45 m, and then became relatively constant from 45 to 90 m. This sill is presumably a reflection of a small scale spatial relationship for these variables. Beyond  $h = 90$  m, however, there was a sharp increase in  $\gamma$ , indicating larger differences between locations and the likely presence of other spatial relationships. The variograms for Cd<sub>g</sub> and LnCl show similarities to those of the natural log of DTPA-extractable Na (LnNa) or the natural log of water-extractable SO<sub>4</sub>-S (LnS) at  $h < 45$  m, but their spatial dependencies become increasingly dissimilar at longer lag distances.

None of the variograms for Cd<sub>g</sub>, LnCl, LnNa, or LnS were bounded by a constant sill, when the entire range of data was considered. For Cd<sub>g</sub> and LnCl, the stationarity assumption was generally satisfied within separation distances of about 90 m, and the variograms were fitted to the spherical model (Table 2). For LnNa and LnS, we attempted to improve the shape of the semivariogram by removing general trend. The original data were modeled by Eq. [2], yielding the surfaces described by the fitted coefficients in Table 3. About 33% of the variability for LnNa and 24% for LnS were modeled by these simple linear surfaces. After removal of the trend, the residual (detrended) values were used to recalculate the semiva-

**Table 2.** Parameters† of the spherical model used to describe omnidirectional-semivariograms for nine variables.

Variable‡	C <sub>0</sub>	C	A
Cd <sub>g</sub>	0.06	0.40	45
Cd <sub>dtpa</sub> §	0.34	0.41	32
Cd <sub>t</sub> §	0.65	0.28	30
pH	0.03	0.83	35
OC§	0.42	0.49	55
CEC	0.13	0.66	35
LnCl	0.08	0.40	45
LnNa§	0.11	0.51	50
LnS§	0.11	0.45	45

† C<sub>0</sub>, nugget variance (relative); C, structural variance (relative); and A, range (m). C<sub>0</sub> and C for each variable are expressed as a fraction of the maximum semivariance for the variable.

‡ Cd<sub>g</sub>, concentration of Cd in grain; Cd<sub>dtpa</sub>, DTPA-extractable Cd; Cd<sub>t</sub>, total Cd; OC, organic C; CEC, cation-exchange capacity; LnCl, LnNa, and LnS are natural logarithms of Cl, Na, and S, respectively.

§ Parameters were derived from the semivariogram of detrended data (see text).

**Table 3. Coefficients<sup>†</sup> of the second-order polynomial equation used to describe overall trend in the spatial distribution of soil characteristics.**

Variable <sup>‡</sup>	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>f</i>	<i>R</i> <sup>2</sup>
LnNa	7.40	$-1.06 \times 10^{-2}$	$-2.92 \times 10^{-2}$			0.326
LnS	7.83	$-1.50 \times 10^{-2}$	$-4.35 \times 10^{-2}$			0.241
Cd <sub>dtpa</sub>	0.085	$9.1 \times 10^{-4}$		$-5.4 \times 10^{-6}$	$1.5 \times 10^{-5}$	0.784
Cd <sub>t</sub>	0.31	$2.26 \times 10^{-3}$	$-1.13 \times 10^{-3}$	$-1.33 \times 10^{-5}$		0.469
OC	29.5	$1.58 \times 10^{-2}$	$-8.9 \times 10^{-2}$			0.133

<sup>†</sup> *a*, *b*, *c*, *d*, and *f* are the coefficients in the second-order polynomial equation (see Eq. [2]), and *R*<sup>2</sup> is the coefficient of determination.

<sup>‡</sup> Cd<sub>dtpa</sub>, DTPA-extractable Cd; Cd<sub>t</sub>, total Cd; OC, organic C; LnNa and LnS are natural logarithms of Na and S, respectively.

riances. This process significantly improved the semivariogram for LnNa, but the improvement for LnS was only slight (Fig. 2). Both of the detrended variograms were fitted to a spherical curve (parameters listed in Table 2) out to 90 m, as was done for Cd<sub>g</sub> and LnCl.

The variograms for Cd<sub>dtpa</sub> and Cd<sub>t</sub> were generally convex. The semivariogram of Cd<sub>dtpa</sub> had a very small nugget variance, followed by a rise to a maximum at about 90 m. The variogram for Cd<sub>t</sub> had a larger nugget variance, but a similar trend (one site with a relatively large value for Cd<sub>t</sub> was excluded, because it significantly distorted semivariances at small lag distances). Neither semivariogram displayed a consistent sill nor satisfied the stationarity assumption. General trend was modeled with Eq. [2], obtaining the fitted parameters of Table 3, which accommodated 78.4% and 46.9% of the variability in Cd<sub>dtpa</sub> and Cd<sub>t</sub>, respectively. The detrended variograms for Cd<sub>dtpa</sub> and Cd<sub>t</sub> were fitted by the spherical model using range distances of 32 and 30 m, respectively, and the nugget and structural variances given in Table 2.

The variogram of OC increased almost linearly with lag distance (Fig. 2), suggesting a linear trend that was modeled by Eq. [2] using the coefficients in Table 3. After removal of this trend, the semivariogram shows a reasonable spherical structure with a range of about 55 m (Detrended OC of Fig. 2).

The semivariogram of CEC increased steadily as *h* increased to about 40 m, but then fluctuated in a periodic pattern. Periodic patterns are often caused by a succession of areas with high and low values (the *hole effect*, Journel and Huijbregts, 1978), which may reflect natural periodicity or other causes (Trangmar et al., 1985; Borges and Mallarino, 1997). No corrections for periodicity were used in modeling the semivariogram for CEC (Table 2, Fig. 2), because the simple spherical model provided a reasonable fit, especially at short-range lag distances which dominated the interpolation process based on the 16 closest points.

The semivariogram of pH was fairly well described throughout the range of the data by the spherical model. The fitted curve for relative semivariance has a small nugget variance, a large structural variance, and a range of 35 m (Table 2, Fig. 2).

We have been unable to find other reports of the spatial variability of Cd in crops nor of measurements of plant-available Cd in soil, but there have been a few studies of Cd<sub>t</sub>. In uncontaminated agricultural soils, Garrett (1994) found that almost all of the variability in Cd<sub>t</sub> in prairie soils was at separation distances of <20 km. His work covered 850 000 km<sup>2</sup> of Canada and an adjoining strip of the northern USA including northern North

Dakota. Our results, at an entirely different scale of study, suggest that substantial variability exists also in the range of meters as well as in kilometers. The spatial variability of Cd<sub>t</sub> in areas of contaminated soils is less pertinent to our work, but is reported to be highly complex, as might be expected from anthropogenic disturbances (Atteia et al., 1994; Boekhold and van der Zee, 1992).

Although data for Cd are limited, evidence is readily available for the spatial dependency of other soil and crop properties at the scale of agricultural field operations (Trangmar et al., 1985; Warrick et al., 1986; West et al., 1989). Several of the characteristics that we measured have been described specifically in other studies of spatial variability. For example, Cahn et al. (1994) reported that after removal of trend the residual data for OC were characterized by a range of about 20 m in a 0.25-ha area in central Illinois. Cambardella et al. (1994) found that pH and OC were strongly correlated with range distances of 104 and 117 m, respectively, in central Iowa. The spatial dependencies of salinity-related characteristics have been described in some detail; e.g., Gallichand et al. (1992) determined a range distance of 120 m for Na adsorption ratio and 90 m for electrical conductivity in a saline area of about 2 ha in southern Alberta. Spatial variability in crop characteristics and crop responses to soil characteristics are common also. For example, Borges and Mallarino (1997) showed that the spatial variability of plant P and K uptake in no-till corn and soybean were both site specific and direction specific. Bhatti et al. (1991) found soil properties and wheat yield had strong spatial dependency with range distances from 70 to 145 m. The studies mentioned above, as well as our own results, show clearly the existence of important and interpretable spatial variability in numerous characteristics of soils or crops at the scale of agricultural field operations.

### Map Preparation, Comparison, and Overlay Analysis

The distributions of crop and soil characteristics in the field are most easily seen when portrayed in maps. Using the fitted parameters of nugget, sill, and range (*C*<sub>0</sub>, *C*, and *A*) in Table 2, we performed block kriging with a block size of 1 by 1 m<sup>2</sup> to obtain interpolated values for all nine variables across the sampled area of 5766 m<sup>2</sup> (i.e., 186 by 31 m<sup>2</sup>). For Cd<sub>dtpa</sub>, Cd<sub>t</sub>, LnNa, LnS and OC, the kriging was performed on the detrended data, after which the trend surfaces (described by Eq. [2] and Table 3) were added to their kriged values to yield the final interpolated values. Maps (Fig. 3) based

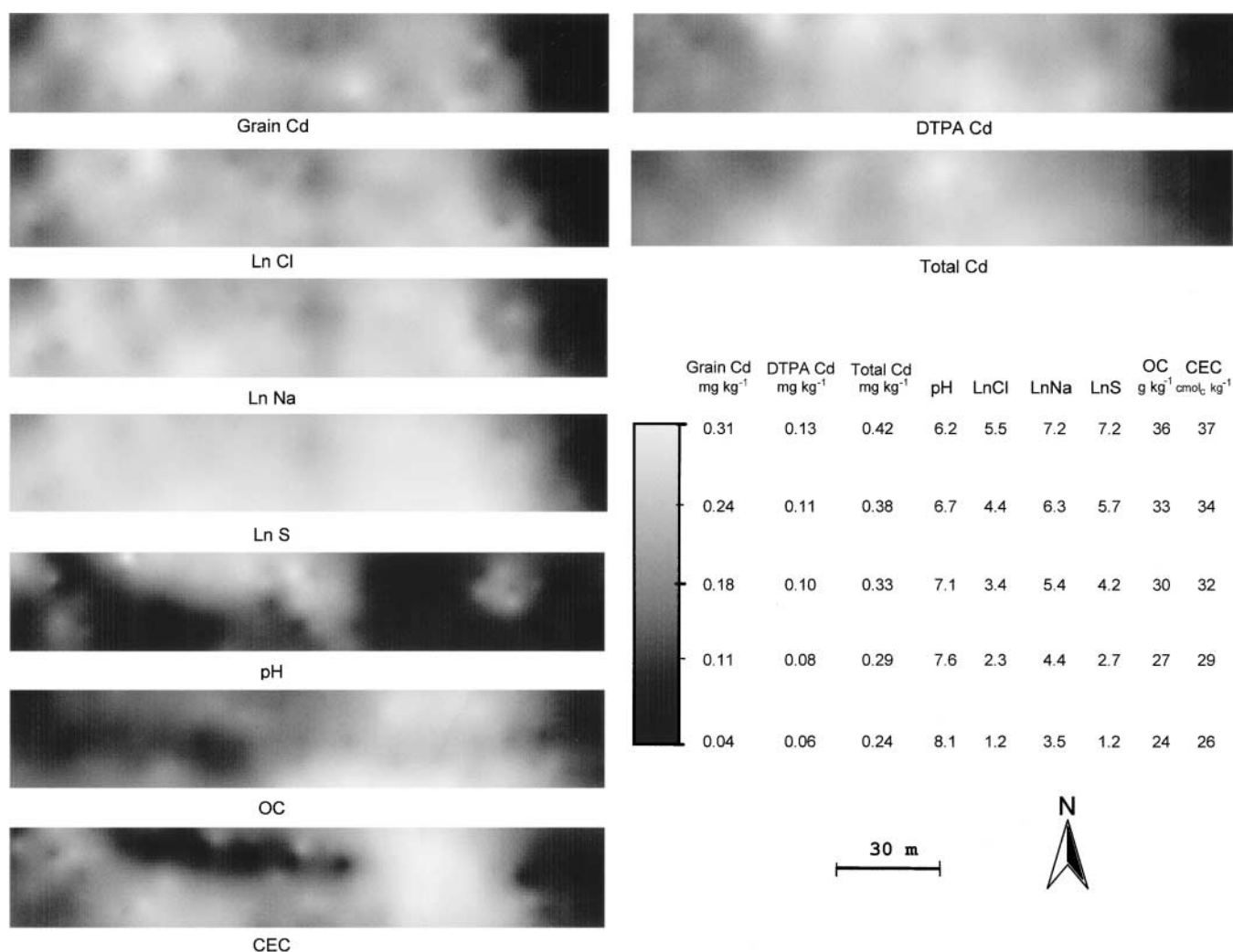


Fig. 3. Maps of grain Cd and eight soil characteristics in a field of durum wheat. The soil characteristics include: DTPA-extractable Cd (DTPA Cd), Total Cd, natural log-transformed water-extractable Cl (LnCl) and SO<sub>4</sub> as S (LnS), natural log-transformed DTPA-extractable Na (LnNa), pH, organic C (OC), and cation-exchange capacity (CEC).

on the final interpolated values were prepared with ARC/INFO (ESRI Inc., 1994).

Figure 3 shows clearly that the nine characteristics of grain or soil were not distributed in a random manner across the field. Most variables showed a pronounced tendency for local clustering of similar values, with gradual changes from areas of low to high values. Grain collected from the Svea soil at the eastern end of the sampled area was generally low in Cd<sub>g</sub>, while samples from the Hamerly or Miranda soils (Fig. 1) were typically much higher. Two areas contained grain with Cd<sub>g</sub> of almost 0.3 mg kg<sup>-1</sup>. One was located in the Hamerly map unit, and the other was found in a transitional area between Hamerly and Miranda units. The map for LnCl shows that the distribution of this characteristic was very similar to that of Cd<sub>g</sub>. Maps for LnS and LnNa were also similar, showing visually the strong association of Cd<sub>g</sub> with all of the salinity-related characteristics. The maps for Cd<sub>dtpa</sub> and Cd<sub>t</sub> are similar in some respects to those for Cd<sub>g</sub> and the variables related to salinity, but the correspondence is clearly less close. The distributions of CEC and OC are reasonably close to each other, but

they are unlike distributions for other characteristics. The map for soil pH does not resemble that for any other characteristic.

In general, the nonsaline Svea soil was characterized by relatively low values for all variables, except for pH. Figure 1 shows that the boundary between the Svea and the more poorly drained soils to the west occurs at about 40 m from the eastern boundary. Many grain and soil characteristics became more dissimilar at, or near, this boundary, which is reflected in the range distances of 30 to 55 m for the nine modeled characteristics. Spatial correlation in soil characteristics is often limited by changes associated with soil boundaries (Trangmar et al., 1985; Webster, 1985). In our data, the range distances for Cd<sub>g</sub>, LnCl, LnS, and LnNa were particularly close to limits set by the Svea-Hamerly boundary, which also separated the saline and nonsaline areas of the field.

Quantitative measures of association among the maps were obtained by correlation and regression using the interpolated values for each 1-m<sup>2</sup> cell. The correlation coefficient between the maps for Cd<sub>g</sub> and LnCl was 0.923 (Table 4). The correlations with the maps for LnNa and

**Table 4. Pearson correlation coefficients among the interpolated maps of grain Cd and selected soil characteristics in a durum wheat field.**

Variable†	Cd <sub>g</sub>	Cd <sub>dtpa</sub>	Cd <sub>t</sub>	pH	OC	CEC	LnCl	LnNa
Cd <sub>dtpa</sub>	0.780							
Cd <sub>t</sub>	0.692	0.858						
pH	-0.193	-0.451	-0.213					
OC	0.220	0.454	0.460	0.186				
CEC	0.461	0.463	0.579	0.405	0.637			
LnCl	0.923	0.801	0.746	-0.044	0.421	0.646		
LnNa	0.877	0.780	0.755	-0.036	0.362	0.659	0.949	
LnS	0.863	0.812	0.793	-0.105	0.436	0.650	0.939	0.973

† Cd<sub>g</sub>, concentration of Cd in grain; Cd<sub>dtpa</sub>, DTPA-extractable Cd; Cd<sub>t</sub>, total Cd; OC, organic C; CEC, cation-exchange capacity; LnCl and LnNa are natural logarithms of Cl and Na, respectively.

LnS were also high. These relationships reflect closely those displayed by the original data (Norvell et al., 2000). The correlation between maps of Cd<sub>g</sub> and Cd<sub>dtpa</sub> was the highest among the nonsalinity factors. The correlation between the maps for Cd<sub>dtpa</sub> and Cd<sub>t</sub> was strong also, reflecting the close association of these soil characteristics (data not shown). Correlations among maps for LnNa, LnCl, and LnS were all very high with the *r* of 0.973 between LnNa and LnS being the highest in the Table. It is interesting to note that all of the above correlations among mapped variables exceed the correlations among the original variables (Norvell et al., 2000). This increase in correlation arises because similarities in the spatial dependencies of these variables enhance the associations among their interpolated values. Conversely, the correlations between the mapped values of pH and those for Cd<sub>g</sub> or Cd<sub>dtpa</sub> are lower than for the original data, because dissimilarities in their spatial dependencies diminish the degree of association in their interpolated values.

Multiple linear regression among maps showed that the best prediction of the Cd<sub>g</sub> map was obtained from the maps for LnCl and Cd<sub>dtpa</sub>.

$$\text{Cd}_g = -0.05 + (0.47 \times \text{Cd}_{\text{dtpa}}) + (0.042 \times \text{LnCl})$$

$$(R^2 = 0.858) \quad [3]$$

This relation among the mapped variables is not surprising in the sense that the same variables provided the best predictions of Cd<sub>g</sub> when the original data set was analyzed (Norvell et al., 2000). However, the increase, mentioned above, in correlations among the mapped values has two effects on this regression. First, the overall *R*<sup>2</sup> of 0.86 for Eq. [3] is higher than the *R*<sup>2</sup> of 0.66 for the corresponding regression using the original data. Second, the importance of LnCl in the mapped data is increased relative to Cd<sub>dtpa</sub> to the extent that the inclusion of Cd<sub>dtpa</sub> improves the regression only slightly. As a result, a simple linear regression using only the map for

LnCl is virtually as effective a predictor of the mapped values of Cd<sub>g</sub> as is Eq. [3].

$$\text{Cd}_g = -0.02 + (0.047 \times \text{LnCl}) \quad (R^2 = 0.851) \quad [4]$$

The distribution of Cd<sub>g</sub> and the eight soil characteristics can be compared with the distribution of mapped soil series by overlaying the field soil map (Fig. 1) with the interpolated maps for these attributes (Fig. 3). A comparison of the means of variables mapped within each soil series shows that differences among these series were significant for most variables (Table 5). However, the mapped characteristics differed less, in general, between the two more poorly drained soils (Miranda and Hamerly) than between either of these soils and the better drained soil (Svea). Differences in Cd<sub>g</sub> and salinity were the most striking. For example, Cd<sub>g</sub> from the Svea was only about 1/3 of that from the Miranda or Hamerly. Differences in soil Cl, Na, or S among the soils were also large and significant. Concentrations of Cd<sub>dtpa</sub> and Cd<sub>t</sub> were lower in the Svea than in the other two map units, but the relative differences were less than for Cd<sub>g</sub>, Cl, Na, or S. Similarly, Li et al. (1994) reported relatively large differences in Cd in soil and sunflower (*Helianthus annuus* L.) seeds among soil series, and also within soil series at locations which differed in Cl.

The uptake and accumulation of Cd by crops is known to be affected by agronomic management (Grant et al., 1999). These activities include crop selection, crop rotation, fertilization with macronutrients or micronutrients (particularly Zn), liming to adjust soil acidity, irrigation, and tillage. In the case of the field which we studied, salinity management or alternative crop selection might well be the most useful options to minimize or avoid the accumulation of Cd in durum grain. Our results show also that different parts of a field may differ quite widely in their need for alternative management practices. Most of the differences in crop and soil characteristics in this

**Table 5. Mean values of grain Cd and selected soil characteristics within areas mapped as separate soil units in a durum wheat field.†‡**

Variable§	Cd <sub>g</sub>	Cd <sub>dtpa</sub>	Cd <sub>t</sub>	pH	OC	CEC	Cl	S	Na
	mg kg <sup>-1</sup>				g kg <sup>-1</sup>	cmol. kg <sup>-1</sup>	mg kg <sup>-1</sup>		
Miranda	0.181a	0.102b	0.32b	7.49b	26.8c	31.3a	129b	692a	655a
Hamerly	0.224a	0.121a	0.37a	7.33b	31.0a	32.3a	271a	908a	754a
Svea	0.067b	0.083c	0.28c	7.73a	28.5b	29.0b	16c	154b	115b

† Map unit: Miranda, fine, smectitic, frigid Leptic Natrustolls; Hamerly, fine-loamy, mixed, superactive, frigid Aeric Calciaquolls; Svea, fine-loamy, mixed, superactive, frigid Pachic Hapludolls.

‡ Means followed by the same letter are not significantly different at the 0.05 probability level.

§ Cd<sub>g</sub>, concentration of Cd in grain; Cd<sub>dtpa</sub>, DTPA-extractable Cd; Cd<sub>t</sub>, total Cd; OC, organic C; CEC, cation-exchange capacity; Cl, water-extractable Cl; Na, soluble Na extracted by DTPA; S, water-extractable SO<sub>4</sub>-S.



field were associated with mapped soil series. Thus, there appears to be potential to use detailed soil information of several types to identify areas within fields where site-specific management would be helpful in achieving a goal such as the reduction of Cd in crops.

## REFERENCES

- American Public Health Association. 1995. Total organic carbon (TOC), combustion-infrared method, Method No. 5310 B. Standard Methods for Examination of Water and Wastewater, 19th ed., Am. Pub. Health Assoc., Washington DC.
- Atteia, O., J. P. Dubois, and R. Webster. 1994. Geostatistical analysis of soil contamination in the Swiss Jura. *Environ. Pollut.* 86:315–327.
- Bhatti, A.U., D.J. Mulla, and B.E. Frazier. 1991. Estimation of soil properties and wheat yields on complex eroded hills using geostatistics and thematic mapper images. *Remote Sensing Environ.* 37: 181–191.
- Boekhold, A.E., and S.E.A.T.M. van der Zee. 1992. Significance of soil chemical heterogeneity for spatial behavior of cadmium in field soils. *Soil Sci. Soc. Am. J.* 56:747–754.
- Borges, R., and A.P. Mallarino. 1997. Field-scale variability of phosphorus and potassium uptake by no-till corn and soybean. *Soil Sci. Soc. Am. J.* 61:846–853.
- Cahn, M.D., J.W. Hummel, and B.H. Brouer. 1994. Spatial analysis of soil fertility for site-specific crop management. *Soil Sci. Soc. Am. J.* 58:1240–1248.
- Cambardella, C.A., T.B. Moorman, J.M. Novak, T.B. Parkin, D.L. Karlen, R.F. Turco, and A.E. Konopka. 1994. Field-scale variability of soil properties in central Iowa soils. *Soil Sci. Soc. Am. J.* 58: 1501–1511.
- Chaney, R.L., J.A. Ryan, Y.M. Li, R.M. Welch, and P.G. Reeves. 1996. Phyto-availability and bio-availability in risk assessment for Cd in agricultural environments. p. 49–78. *In* Sources of cadmium in the environment. Organization for economic co-operation and development, (OECD) publications service. Paris, France.
- Chapman, H.D. 1965. Cation-exchange capacity. p. 891–913. *In* C.A. Black (ed.) Methods of soil analysis, Part 2, 1st ed. Agron. Monogr. 9. ASA, Madison, WI.
- Clarke, J.M., D. Leisle, and G.L. Kopytko. 1997. Inheritance of cadmium concentration in five durum wheat crosses. *Crop Sci.* 37: 1722–1726.
- Codex Alimentarius Commission. 1999. Report of the thirty-third session of the Codex committee on food additives and contaminants. *In* ALINORM 99/12A, Twenty-third Session, Joint FAO/WHO Food Standards Programme, 28 June–3 July, 1999, Rome, Italy. Food and Agriculture Organization of the United Nations, The Hague, and the World Health Organization, Rome, Italy.
- Council of Europe. 1994. Lead, cadmium and mercury in food: Assessment of dietary intakes and summary of heavy metal limits of foodstuffs. Council of Europe Press, Strasbourg, France.
- ESRI Inc. 1994. ARC/INFO Grid manual. ESRI Inc. Redlands, CA.
- Gallichand, J., G.D. Buckland, D. Marcotte, and M.J. Hendry. 1992. Spatial interpolation of soil salinity and sodicity for a saline soil in Southern Alberta. *Can. J. Soil Sci.* 72:503–516.
- Garrett, R.G. 1994. The distribution of cadmium in A horizon soils in the prairies of Canada and adjoining United States. p. 73–82. *In* Current Research 1994-B. Geological Survey of Canada, Ottawa, Canada.
- Goovaerts, P. 1997. Geostatistics for natural resources evaluation. Oxford University Press, New York.
- Grant, C.A., L.D. Bailey, M.J. McLaughlin, and B.R. Singh. 1999. Management factors which influence cadmium concentrations in crops. p. 151–198. *In* M.J. McLaughlin and B.R. Singh (ed.) Cadmium in soils and plants. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Holmgren, G.G.S., M.W. Meyer, R.L. Chaney, and R.B. Daniels. 1993. Cadmium, lead, zinc, copper, and nickel in agricultural soils of the United States of America. *J. Environ. Qual.* 22:335–348.
- Journel, A.G., and Ch. Huijbregts. 1978. Mining geostatistics. Academic Press, London.
- Li, Y.M., R.L. Chaney, and A.A. Schneiter. 1994. Effect of soil chloride level on cadmium concentration in sunflower kernels. *Plant Soil.* 167:275–388.
- Lindsay, W.L., and W.A. Norvell. 1978. Development of a DTPA soil test for zinc, iron, manganese, and copper. *Soil Sci. Soc. Am. J.* 42:421–428.
- McLaughlin, M.J., L.T. Palmer, K.G. Tiller, T.A. Beech, and M. K. Smart. 1994. Increased soil salinity causes elevated cadmium concentrations in field-grown potato tubers. *J. Environ. Qual.* 23: 1013–1018.
- NRCS. 2001. National SSURGO database [Online]. Available at <http://www.ftw.nrcs.usda.gov/cgi-bin/login.pl> (verified 25 July 2001). USDA–NRCS.
- Norvell, W.A., J. Wu, D.G. Hopkins, and R.M. Welch. 2000. Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. *Soil Sci. Soc. Am. J.* 64:2162–2168.
- SAS Institute Inc. 1988. SAS/STAT user's guide. Release 6.03 ed. SAS Institute, Inc., Cary, NC.
- Simmons, M., and D. Moos. 1990. Soil Survey of Cavalier County, North Dakota. USDA-SCS in cooperation with North Dakota Agric. Exp. Stn, North Dakota Cooperative Ext. Service, North Dakota State Soil Conserv. Comm. U.S. Gov. Print. Office, Washington, DC.
- Stein, A., J. Brouwer, and J. Bouma. 1997. Methods for comparing spatial variability patterns of millet yield and soil data. *Soil Sci. Soc. Am. J.* 61:861–870.
- Taylor, P.J. 1982. Quantitative methods in geography: An introduction to spatial analysis. Houghton Mifflin, Boston, MA.
- Timlin, D.J., Ya. Pachepsky, V.A. Snyder, and R.B. Bryant. 1998. Spatial and temporal variability of corn grain yield on a hillslope. *Soil Sci. Soc. Am. J.* 62:764–773.
- Trangmar, B.B., R.S. Yost, and G. Uehara. 1985. Application of geostatistics to spatial studies of soil properties. *Adv. Agron.* 38:45–94.
- van Es, H.M. 1993. The spatial nature of soil variability and its implications for field studies. p. 27–36. *In* S.A. Levin et al. (ed.) Patch Dynamics. Springer Verlag, Berlin, Germany.
- Wagner, G.J. 1993. Accumulation of cadmium in crop plants and its consequences to human health. *Advances in Agronomy* 51:173–212.
- Warrick, A.W., D.E. Myers, and D.R. Nielsen. 1986. Geostatistical methods applied to soil science. p. 53–82. *In* A. Klute (ed.) Methods of soil analysis. Part 1, 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- Webster, R. 1985. Quantitative spatial analysis of soil in the field. *Adv. Soil Sci.* 3:1–70.
- West, C.P., A.P. Mallarino, W.F. Weding, and D.B. Marx. 1989. Spatial variability of soil chemical properties in grazed pastures. *Soil Sci. Soc. Am. J.* 53:784–789.
- Wolnik, K.A., F.L. Fricke, S.G. Capar, M.W. Meyer, R.D. Satzger, and E. Bonnin. 1983. Elements in major raw agricultural crops in the United States. 1. Cadmium and lead in lettuce, peanuts, potatoes, soybeans, sweet corn, and wheat. *J. Agric. Food Chem.* 31: 1240–1244.